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BOROSILICATE MICROPOROUS GLASSES FOR REVERSE OSMOSIS

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The characteristics of microporous borosilicate glasses are described. Glasses with an optimum pore distribution are recommended for production and application.

Researchers are currently developing porous glasses that are free from the drawbacks typical of other porous materials used in reverse osmosis. Porous glasses are characterized by high reliability and temperature resistance, which makes it possible to separate aggressive solutions and perform chemical and thermal sterilization, and by rigidity of structure, including shrinkage at working pressures; they can be conveniently stored and transported in the dry state, etc.

A borosilicate glass is subjected to thermal treatment for several hours at a temperature of $450-600^{\circ}\mathrm{C}$. The thermal treatment schedule depends on the composition and thickness of the particular glass. This is usually determined visually. Cooling is followed by leaching in mineral acids, after which a porous structure consisting mostly of SiO_2 remains. A special technique of phase separation and pickling was implemented. Since glasses only in a certain range of compositions tend to modify their residual silicate structure in the course of pickling of the borate-rich soluble phase, porous glasses were produced from alkali-borosilicate glass of the following composition (wt.%) 73-76 SiO_2 , 1-2 $\mathrm{Al}_2\mathrm{O}_3$, 14-17 $\mathrm{B}_2\mathrm{O}_3$, 3-4 $\mathrm{Na}_2\mathrm{O}$, and 5-6 PbO. However, the production of a precise glass composition in practice is impeded by the volatility of $\mathrm{B}_2\mathrm{O}_3$ and $\mathrm{Na}_2\mathrm{O}$.

The present study presents the results of studying porous glasses with pore sizes of 18-28, 50-54, and over 100 Å. The permeability of glasses was measured based on the quantity of liquid transmitted per time unit relative to the working surface area of the glass. The initial solutions were aqueous solutions of different salts. The studies were carried out using a specially designed set [1,2] at a pressure of 15 MPa and more. It is found that the glass structure does not change with time, and its permeability remains constant after 4-5 h of operation at the specified pressure. The rigidity of the glass structure is corroborated by the absence of the permeability hysteresis loop with consecutive increase and decrease in the working pressure. It can be seen in Fig. 1 that

the dependences of glass permeability on the initial solution pressure are linear and can be described by the equation

$$G = A [p - (P_1 - P_2)],$$

where G is the permeability; p is the excessive pressure applied to the solution separated; P_1 and P_2 are the osmotic pressures of the initial solution and the filtrate, respectively.

It should be noted that the permeability of glass satisfying the conditions of the equation corroborates the reliability of its porous structure. This conclusion can be extrapolated to other porous materials with a rigid structure.

The results of the experiment indicated that preliminary treatment of porous glasses with AlCl₃ solution stabilizes the work of the membranes. A similar effect was observed in the course of an earlier study, when after separating solutions of different types of dissolved compounds a short-time separation of AlCl₃ solution was performed. The AlCl₃ solution was used as a reference one together with NaCl solution. At the same time, this salt was used in different time and temperature conditions with different concentrations of dissolved compounds. The time of experiments with AlCl₃ solu-

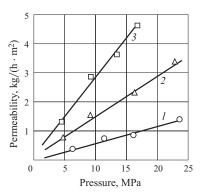


Fig. 1. Dependence of the permeability of membranes with an average pore diameter of 18 - 28 Å (*I*), 50 - 54 Å (*2*), and over 100 Å (*3*) on the pressure of initial 0.1-M initial AlCl₃ solution.

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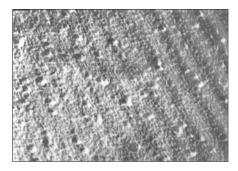


Fig. 2. Structure of the surface of capillary-porous membranes $(\times 200,000)$.

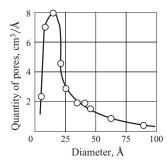


Fig. 3. Distribution of pores over diameter of capillary-porous membranes

tion was sufficient to obtain a stable operation of the membranes. The further stabilizing action of AlCl₃ was confirmed by adsorption and desorption isotherms when determining the porosity of glasses in washing and drying, after which the pore distribution was measured using mercury porometry, adsorption, and electron-microscopic methods.

The size distribution of pores in glasses was determined experimentally. The highest distribution of small-radius pores was 9.5 Å. Hence is follows that the pore radii varied so insignificantly that one can justifiably speak of the stable structure of porous glass.

The parameters of the pore structure of glasses preliminarily treated with 0.1 M solution of AlCl₃ and subjected to a long (700 h) testing are identical to the pore structure parameters of the membranes that did not participate in testing. It was found that the pore structure is very stable. The absence of any significant changes in the volume of pores of different sizes corroborates the validity of these conclusions.

Figure 2 shows the structure of the surface of porous glasses (an electron microphoto of a glass replica after heat treatment for 24 h at 540° C exhibits fragments of uniform structure of width 30-70 Å).

As a consequence of the experiments, the chemical resistance and strength of porous glasses have been determined.

TABLE 1

Initial solution	Initial solu- tion temper- ature, °C	Selectivity,	Permeability, 10^{-3} liter/(h · m ²)	Viscosity, mPa · sec
NaCl, 58.5×10^{-3} M	18.0	74.5	291.6	1.056
	36.3	78.7	427.8	0.704
$Al(NO_3)_3$, 0.107 M	18.8	82.2	78.2	1.035
	40.0	92.3	130.3	0.656

TABLE 2

Concentration of initial solution Al(NO ₃) ₃ , M	Initial solution tempera- ture, °C	Permeability, liter/(h · m ²)		Selectivity, %	
		estimated values	experimen- tal data	estimated values	experimen- tal values
0.213	22	0.21	0.20	78.9	79.3
	27	0.23	0.23	77.8	81.0
	32	0.26	0.27	82.0	77.5
0.534	22	0.14	0.14	70.4	71.8
	27	0.15	0.18	72.9	70.2
	32	0.17	0.20	74.5	68.6

Table 1 shows experimental data confirming that an increase in the temperature of the initial solution improves the parameters of solution separation by porous glasses. A comparison of separation parameters based on the developed equations [1] and those obtained in experimental studies (Table 2) confirms the stability of membrane operation. Figure 3 shows the pore-size distribution. The maximum distribution is observed in a range of $15-20\,\text{Å}$ and in general from 13 to 40 Å. At the same time, a substantial amount of large-diameter pores is registered. It can be expected that decreasing the quantity of coarse pores will improve the separation parameters and, in particular, will increase the selectivity of separation by porous glasses.

Therefore, to improve the parameters of separation by porous glasses, it is necessary to modify the production technology in order to avoid such pores.

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